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(54) Silicone/organic copolymer emulsions

(57) Disclosed herein is the emulsion copolymerizing of a particular crosslinker, i.e., either a siloxane or silazane, with an organic monomer. An emulsion is formed therefrom having particles consisting of polymer chains formed from an organic monomer. Depending on the crosslinker and reaction conditions, these emulsion polymer chains are either crosslinked or uncrosslinked. The uncrosslinked polymer chains are then crosslinked at a later point by the addition of a suitable catalyst.

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Description

This invention relates to the preparation of polymer latices and to the polymers derived therefrom. This invention also introduces silicone functional polymer latices which condense into stable crosslinked films upon the evaporation of water.

"Polymer latices" are well known in the art and refer to aqueous dispersions of a water-insoluble polymer which is present in the form of very fine particles. Polymer latices are often called aqueous emulsion polymers.

Polymer latices have wide utility as intermediates for surface coating compositions. They are often employed as adhesives and film forming agents in paint compositions for all types of applications.

Those skilled in the art have attempted to prepare polymers incorporating siloxane functionality by utilizing alkoxy silanes or alkoxy silane derivatives. U.S. Patent 3,294,725 claims the aqueous emulsion polymerization of organosiloxanes and silcarbanes without using strong bases or strong mineral acids as the polymerization agent and without using a separate emulsifying agent. This patent achieves emulsion polymerization using a combined surface active sulfonic acid catalyst, such as dodecylbenzene sulfonic acid (DBSA). However, it is limited to the homopolymerization of organosiloxanes and silcarbanes and the copolymerization of various types of organosiloxanes with each other or with silcarbanes.

U.S. Patent 3,449,293 discloses the emulsion polymerization of organosilanes with unsaturated monomers and, more particularly, of alkoxy silanes with acrylic esters to produce solid polymers. These solid polymers are insoluble in common organic solvents. This insolubility indicates that the polymers are substantially crosslinked. The solid polymers are disclosed as possessing improved thermal stability as compared with non-crosslinked polymers formed from the polymerization of corresponding unsaturated monomers without siloxane incorporation. The emulsion copolymerization mechanism is a simultaneous addition and condensation reaction initiated using conventional water soluble free radical initiator of the peroxide type, a redox initiator system and emulsifier.

U.S. Patent 3,575,910 is also directed to the preparation of siloxane-acrylate copolymers and aqueous emulsions containing these polymer particles. The copolymers contain 25 to 90 weight percent (wt%) acrylate and 10 to 75 wt% of a siloxane copolymer formed from 45 to 65 mole percent of D type (R_2SiO) monomer and 35 to 55 mole percent of T type ($RSiO_{3/2}$) monomer. Preferably the siloxane-acrylate copolymer is formed by a two stage emulsion polymerization involving first forming the siloxane copolymer and secondly polymerizing the acrylate monomers in the presence of, and onto, said siloxane copolymer. An alternate method (Example 13) of this patent is disclosed whereby the acrylate and siloxane monomers are simultaneously polymerized using stepwise addition of a free radical initiator and a buffer, but without the addition of a strong acid catalyst.

U.S. Patent 3,706,697 discloses a free radical initiated aqueous emulsion polymerization of 55 to 90 percent by weight of an acrylic ester, from 0.5 to 6 percent by weight of gamma-methacryloxypropyltrimethoxy silane (MATS) or gamma-acryloxypropyltrimethoxy silane and from 9.5 to 44.5 weight percent of another copolymerizable free radical initiated monomer which does not have siloxane functionality.

U.S. Patent 3,729,438 shows emulsion polymers containing siloxane functionality formed from copolymers of vinyl acetate and a vinyl hydrolyzable silane, such as for example, MATS or vinyltrimethoxysilane (VTMS). These copolymers are disclosed as capable of post-crosslinking by means of the hydrolyzable siloxane functionality and the means disclosed to retard premature condensation crosslinking is through pH control of the aqueous emulsion within the range of pH 3.5 to 6.

Excessive premature crosslinking of siloxane-containing emulsion polymers was the problem addressed in "Feasibility of Using Alkoxy Silane-Functional Monomers for the Development of Crosslinking Emulsions", T. R. Bourne, B. G. Bufkin, G. C. Wildman and J. R. Grave, Journal of Coatings Technology, Vol. 54, No. 684 January 1982. The authors acknowledge the inability to suppress the hydrolysis-condensation reaction of alkoxy silanes to acceptable levels despite optimizing reaction conditions to provide stable colloidal systems. To provide crosslinkable functionality with greater resistance to hydrolysis, the authors proposed using vinyl-type monomers with more sterically hindered alkoxy silane groups, such as gamma-methacryloxy propylmethyldiethoxy silane (gamma-MAPMDES). However, because of the inability to prevent time dependent and implacable hydrolysis of the (alkyl-O-Si) bond in an aqueous environment, the authors concluded that the use of such sterically hindered alkoxy silane monomers, including gamma-MAPMDES, is limited mainly to applications requiring pre-crosslinked emulsion systems. The final conclusion of the article was, if alkoxy-silane functional emulsions are to achieve the more ubiquitous status sought by industry for an advanced-generation system, then hydrolysis-resistant monomers or aqueous barrier techniques must be developed to prevent premature crosslinking of the alkoxy silane moiety.

Two patents which rely on the crosslinking of siloxane moieties in emulsion copolymers are U.S. Patent 3,898,300 and EPA 0153600. The U.S. patent describes that the incorporation of crosslinked polyorganosiloxane particles into a styrenic copolymer matrix will improve the impact strength of the polymer. The European publication revelas that the emulsion polymerizing of siloxanes with film forming monomers will provide coatings with crosslinked polyorganosiloxane microparticles which act as rheology modifiers for solvent based formulations.

U.S. Patent 5,214,095 teaches copolymers prepared by a concurrent free radical and cationic initiated emulsion

polymerization of at least one free radical initiatable monomer, at least one linear siloxane precursor monomer and at least one bifunctional silane monomer having both free radical polymerizable and silicon functional groups.

However, none of the aforementioned patents or articles suggest our method of preparing our useful emulsion polymers.

The present invention also relates to silicone organic latexes and the compositions resulting therefrom. We have discovered that by emulsion copolymerizing a particular crosslinker, i.e., either a siloxane or silazane, with an organic monomer, unexpectedly superior emulsions result. According to the invention, an emulsion is formed having particles consisting of polymer chains formed from an organic monomer. Depending on the crosslinker and reaction conditions, these emulsion polymer chains are either crosslinked or uncrosslinked. The uncrosslinked polymer chains are then crosslinked at a later point by the addition of a suitable catalyst.

This invention is accomplished by forming an emulsion polymer from organic monomers and by adding a crosslinker. The crosslinker is copolymerized with the organic monomer at any point during the emulsion polymerization of the organic monomer. For instance, the crosslinker is added to the emulsion with the organic monomer but before the emulsion polymerization begins. Alternatively, the crosslinker is added at a point after most of the organic monomer has been polymerized or at any point during the emulsion polymerization.

While not wishing to be bound by any particular theory, we believe that under the proper conditions, the Si-O-Si or Si-NR-Si bonds of the crosslinker are cleaved by water to produce a SiOH functionalized organic latex. This is best accomplished by running the emulsion polymerization at a pH of from 1 to 4 and at a temperature of from 50°C. to 90°C. The SiOH functionalized latex having silicone organic polymer chains is crosslinked later with the addition of an appropriate catalyst, most likely an organo-tin catalyst.

In the present invention, the crosslinker comprises 0.1 to 20 parts by weight of the polymer latex. The total solids content of the latex ranges from 20 weight percent up to 60 weight percent. When essentially all the water is removed from our composition, whether crosslinked or uncrosslinked, it is capable of condensing into a clear, stable, crosslinked, polymeric film.

In summation, we teach a silicone functional polymer latex, which may under certain conditions be crosslinked and which under other conditions will remain uncrosslinked until a catalyst is added. We also claim a latex suitable for use in curable coatings, paints, caulks, adhesives, non-woven and woven fabrics, ceramic compositions and as modifiers, processing aids or additives in thermoplastics, cements and asphalts. The crosslinked polymeric films derived from our polymer latices are suitable for use in these applications.

The polymer latices of this invention are compositions having:

100 parts by weight of organic monomer,
0.25 to 7 parts by weight of surfactant,
0.1 to 2 parts by weight of initiator,
60 to 400 parts by weight of water, and
0.1 to 20 parts by weight of crosslinker having the formula:

$$Q_nR_{3-n}Si\text{-}X\text{-}(RQSiX)_z(R_2SiX)_y\text{-}SiR_{3-n}Q_n$$

or

$$\boxed{(RQSiX)_{z'},(R_2SiX)_{y'}}$$

where:

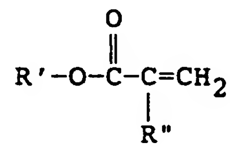
Q independently represents an allyl, vinyl, hexenyl, acryloxy or methacryloxy radical;

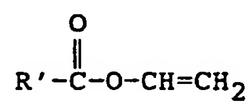
X is O or NR; and
R is independently a hydrogen atom or an alkyl, aryl and alkyl/aryl group having 1 to 8 carbon atoms;
n = 0, 1, 2 or 3;
z = 0 to 200;
y = 0 to 200, with the proviso that if n=0, then $z \geq 1$;
z'= 1 to 50; and
y'= 0 to 50, with the proviso that

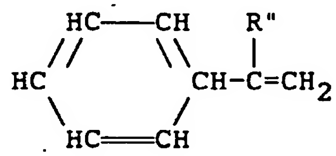
$$\underline{z}' + \underline{y}' \geq 3.$$

Our invention is made by forming an emulsion from constituents including the organic monomer, water and surfactant, such that the organic monomer forms the discontinuous phase and then copolymerizing the organic monomer with a crosslinker.

The organic monomers employed to prepare the emulsion polymer of the present invention are monomers of the formula:



 or



where

R' is an alkyl group having 1 to 20 carbon atoms; and
R" is a hydrogen atom or an alkyl group having 1 to 8 carbon atoms.

Examples of useful monomers are vinyl acetate, styrene, α-methyl styrene, ethyl acrylate, n-butyl acrylate, tertiary butyl acrylate, isobutyl acrylate, amyl acrylate, ethyl butyl acrylate, 2-ethylhexyl acrylate, octyl acrylate, nonyl acrylate, decyl acrylate, tridecyl acrylate, tetradecyl acrylate, hexadecyl acrylate and octadecyl acrylate. The preferred monomers are ethyl acrylate, butyl acrylate and vinyl acetate.

While it is preferred to employ only one organic monomer at one time, if desired, the polymer latices can be prepared using mixtures of two or more different organic monomers. Such compounds are intended to be covered by the terms polymer latice or emulsion polymer as used herein.

Our organic monomer is polymerized in water in the presence of a surfactant. Any conventional anionic or nonionic surfactant, or mixtures thereof, is used in this invention. Such surfactants are well know in the art and are found more fully enumerated in "Synthetic Detergents" by J. W. McCutcheon, MacNair-Dorland Company, New York. Examples of such surfactants are the alkali metal salts of rosin acids, alkali metal and ammonium salts of long chain alkyl sulfates and sulfonates. The alkylene oxide condensates of long chain alcohols and fatty acids also have utility as surfactants herein. Among the preferred surfactants are the alkoxylated condensates of alkyl phenols, such as ethylene oxides of octyl and nonyl phenol; alkoxylated condensates of alcohols, such as ethylene oxides of lauryl alcohol; and the alkali metal alkyl sulfonates, such as sodium lauryl sulfonates. In some instances, it is preferred to employ both anionic and nonionic surfactants to help control particle size of the polymer. The amount of surfactant employed in our invention ranges from 0.25 to 7 parts by weight based on 100 parts by weight of solid polymer in the latex. A more preferred surfactant is TRITON™ X-200 (available from Union Carbide of Danbury, Ct.), which is an aqueous solution of an alkylaryl polyether sodium sulfonate.

The amount of water present in our system is that amount sufficient to produce a polymer latex haying a polymer solids content of from 20 to 60 weight percent. This will correspond to from 60 to 400 parts by weight of water.

An initiator is necessary to begin our emulsion polymerization and any free radical initiator or mixtures thereof, conventionally known in the art are employed. Specific examples are the inorganic peroxides such as hydrogen peroxide, ammonium persulfate and potassium persulfate; organic peroxy catalysts such as the dialkyl peroxides, e.g., diethyl peroxide, diisopropyl peroxide, dilauryl peroxide, dioleyl peroxide, distearyl peroxide, di-(t-butyl) peroxide, di-(t-amyl) peroxide and dicumyl peroxide; the alkyl hydrogen peroxides such as t-butyl hydroperoxide, t-amyl hydroperoxide, cumene hydroperoxide and diisopropyl benzene hydroperoxide; the symmetrical diacyl peroxides, such as acetyl peroxide, propionyl peroxide, lauroyl peroxide, stearoyl peroxide, malonyl peroxide, succinoyl peroxide, phthaloyl peroxide

and benzoyl peroxide; ketone peroxides such as methyl ethyl ketone peroxide or cyclohexanone peroxide; the fatty oil acid peroxides, such as coconut oil acid peroxides; the unsymmetrical or mixed diacyl peroxides, such as acetyl benzoyl peroxide or propionyl benzoyl peroxide; the azo compounds, such as azobisisobutyramidine hydrochloride, 2,2-azobis(isobutylronitrile), 2,2-azobis(2-methylbutyronitrile) and 1,1-azobis(1-cyclohexanecarbonitrile); disulfide; a redox catalytic system (i.e., a catalyst and a reductant), such as sulfate-sulfites, sulfate-sulfoxylate formaldehyde and peroxysulfites. These are more particularly represented by potassium persulfate, sodium metabisulfite, potassium persulfate, sodium or zinc sulfoxylate formaldehyde, t-butyl hydroperoxide, sodium metabisulfite, potassium persulfate and sodium thiosulfate. Mixtures of such catalysts may also be employed. Obviously only a catalytic amount of the initiator need be employed. Generally, amounts of initiator ranging from 0.1 to 2.0 parts by weight, based on 100 parts by weight of organic monomer in the latex, are sufficient for most purposes. The more preferred initiator herein is ammonium persulfate. Redox catalyst systems are often useful in speeding up the rate of polymerization of the monomers and/or in reducing the temperature of the polymerization process. In this invention, the polymerization of monomers may be carried out in a closed vessel, in an inert atmosphere, under artificially induced pressure or in an open vessel under reflux at atmospheric pressure.

When desirable to conduct our emulsion polymerization at a pH above 1-2, a buffer compound is used. Any conventional buffering agent or mixtures of such agents known in the art, is employed such as sodium acetate, sodium bicarbonate and the like. Generally, amounts of buffer from 1.0 part by weight or less, based on 100 parts by weight of organic monomer in the latex, will be sufficient for most purposes.

While not essential, it is sometimes desirable to include a small amount of chain transfer agent during our polymerization to control the molecular weight of the polymer. Examples of such agents include alkyl mercaptans such as nonyl mercaptan and the like and alkyl halides such as carbon tetrabromide. For a discussion on chain transfer agents during free radical polymerization, see <u>Principles of Polymerization</u>, second edition, George Odian, Wiley and Sons, New York, NY, pages 233-238.

The preparation of emulsion polymers is well known in the art and they can be prepared by a variety of methods. These methods are employed in our invention and are generally taught in the <u>Encyclopedia of Polymer Science and Engineering</u>, Vol. 6, p. 1-51 (1986, Wiley & Sons). Typically, our organic monomers are stirred into a water solution containing a surface active agent or surfactant and a water soluble free radical initiator such as ammonium persulfate. After polymerizing, the system consists of finely divided submicrometer particles that are stabilized in water.

In this invention, a crosslinker is added to the reaction at a predetermined point. The crosslinkers are of the formulae:

$$Q_nR_{3-n}Si\text{-}X\text{-}(RQSiX)_z(R_2SiX)_y\text{-}SiR_{3-n}Q_n$$

or

$$\boxed{(RQSiX)_{z'}(R_2SiX)_{y'}}$$

where:

Q independently represents an allyl, vinyl, hexenyl, acryloxy or methacryloxy radical;
X is O or NR; and
R is independently a hydrogen atom or an alkyl, aryl and alkyl/aryl group having 1 to 8 carbon atoms;
$\underline{n}$ = 0, 1, 2 or 3;
$\underline{z}$ = 0 to 200;
$\underline{y}$ = 0 to 200, with the proviso that if $\underline{n}$=0, then $\underline{z} \geq 1$;
$\underline{z}'$= 1 to 50; and
$\underline{y}'$= 0 to 50, with the proviso that

$$\underline{z}' + \underline{y}' \geq 3.$$

The crosslinker is added in an amount from 0.1 to 20 parts, per 100 parts by weight of the organic monomer and preferable amounts are from 0.5 to 2.0 parts. The preferred crosslinkers are divinyltetramethyldisiloxane, divinyltetramethyl disilazane, methylvinylcyclosiloxane and methylvinylcyclosilazane.

In addition to the above-described reactants, other additives known in the art may also be added, such as amorphous silica, colloidal silica, crystalline silica, clays, aluminum silicate, mica, calcium carbonate, titanium dioxide, alumi-

num oxide, carbon black or zinc oxide. These additives or fillers are added at any point in our method, but are preferably added after all the organic monomer and crosslinker have been polymerized.

A preferred method of producing our emulsion polymer is as follows. Water, surfactant such as TRITON™ X-200, an initiator (ammonium persulfate) and a buffer (sodium bicarbonate) are first mixed together and then agitated for 30 minutes at room temperature using a nitrogen purge. Inhibitor-free monomer (prepared by passing the monomer through activated alumina) is next added to the above reaction mixture all at once. The agitation is maintained and heating is started until an exotherm occurs. The heating is then stopped. When a temperature maximum is obtained, heat is reapplied to the reaction mixture. After the temperature stabilizes, additional monomer is added slowly, preferably dropwise over a two hour period while the reaction temperature is maintained. At some point after 1/3 of the monomer is added, the crosslinker is added along with the remainder of monomer. The final product of our preferred process results in an emulsion polymer used in the practice of this invention. If the reaction is run at a pH of 7 or greater using a buffer system, the resulting polymer chains in the emulsion are crosslinked. If the reaction is run at a pH below 7 and particularly if the reaction is run at pH of 2 and a temperature of from 70-90°C., the resulting polymer chains are uncrosslinked.

While not wishing to be bound by any particular theory, we believe that under controlled conditions, i.e., pH below 5, the Si-O-Si bonds or Si-N-Si bonds of the crosslinker will cleave during emulsion polymerization to form Si-OH bonds. The Si-OH functionality between different polymer chains is then condensed, either on their own or by the addition of an organotin catalyst and/or similar additive.

Our organotin catalyst, used for the post crosslinking step, is an organic salt of tin and is illustrated by tin (II) carboxylates, such as stannous oleate and stannous naphthanate; dialkyl tin (IV) carboxylates, such as dibutyltin diacetate and dibutyltin dilaurate; and tin (IV) stannoxanes, as exemplified by the structure $(Bu)_2SnCl\text{-}O\text{-}(Bu)_2OH$, in which Bu denotes a butyl radical, as taught in U.S. Patent 5,034,455. In preferred embodiments, this catalyst is stannous octoate.

In addition to introducing organotin catalyst to crosslink our uncrosslinked polymer latex, an additive may be added which also facilitates the crosslinking. This additive is added in an amount of 0.1 to 20 parts per wieght of additive and is of the formulae $R_aSiX'_{4-a}$ or $X'_{3-a}R_aSiO\text{-}(R_2SiO)_n\text{-}SiR_aX'_{3-a}$ where R is independently the same or different monovalent hydrocarbon group having from 1-8 carbon atoms; X'is any hydrolyzable group; and <u>a</u> is either 0, 1 or 2.

X' is any hydrolyzable group. The term "hydrolyzable group" means any group attached to silicon which is hydrolyzed by water at room temperature. The hydrolyzable group X' includes hydrogen atom; halogen atoms such as F, Cl, Br or I; groups of the formula -OY, when Y is any hydrocarbon or halogenated hydrocarbon group, such as methyl, ethyl, isopropyl, octadecyl, allyl, hexenyl, cyclohexyl, phenyl, benzyl and beta-phenylethyl; any hydrocarbon ether radical such as 2-methoxyethyl, 2-ethoxyisopropyl, 2-butoxyisobutyl, p-methoxyphenyl or $-(CH_2CH_2O)_2CH_3$; and any N,N-amino radical such as dimethylamino, diethylamino, ethylmethylamino, diphenylamino or dicyclohexylamino. X' can also be any amino radical such as NH_2, dimethylamino, diethylamino, methylphenylamino or dicyclohexylamino; any ketoxime radical of the formula $-ON{=}CM_2$ or $-ON{=}CM'$, in which M is any monovalent hydrocarbon or halogenated hydrocarbon radical such as those shown for Y above and M' is any divalent hydrocarbon radical both valences of which are attached to the carbon, such as hexylene, pentylene or octylene; ureido groups of the formula $-N(M)CONM''_2$ in which M is as defined above or hydrocarbon radical such as those shown for Y above and M" is H or any of the M or M' radicals; carboxyl groups of the formula -OOCMM" in which M and M" are as defined above; or halogenated hydrocarbon radicals as illustrated for Y above; or carboxylic amide radicals of the formula -NMC=O(M") in which M and M" are as defined above. X' can further be the sulfate group or sulfate ester group of the formula $-OSO_2(OM)$ where M is as defined above; hydrocarbon or halogenated hydrocarbon radical as illustrated for Y above; the cyano group; the isocyanate group; and the phosphate group or phosphate ester group of the formula $-OPO(OM)_2$ in which M is as defined above.

The most preferred hydrolyzable groups of this invention are alkoxy groups. Examples of these alkoxy groups are methoxy, ethoxy, propoxy, butoxy, isobutoxy, pentoxy, hexoxy and 2-ethylhexoxy; alkoxyalkoxy radicals such as methoxymethoxy or ethoxymethoxy; and alkoxyaryloxy radicals such as ethoxyphenoxy. The most preferred alkoxy groups are methoxy or ethoxy.

Silane monomers, as well as methods for their preparation, are well known in the art. The silanes employed herien are, for example, vinyltrimethoxysilane, vinyltriethoxysilane, vinyldimethylethoxy-silane, gammamethacryloxypropylmethyldiethoxysilane, vinylmethyldimethoxysilane, vinylmethyldiethoxysilane, vinyltris (2-methoxyethoxy) silane, gamma-methacryloxypropyltrimethoxysilane and vinyltriacetoxysilane.

The polymer latices of this invention have a wide degree of utility in surface coatings, paints, stains, sealants and adhesives. The instant polymer latices are particularly unique in that the polymers form crosslinked coatings merely upon drying, i.e., removal of the water from the polymer latex. The crosslinked protective polymeric films derived from our polymer latices are insoluble in toluene, water and acetone and they exhibit excellent water and solvent resistance. In addition, they are very durable and have a very high degree of scrub resistance. They are particularly useful as additives for high pigment concentrations of paint formulations. When used unpigmented, our crosslinked films produce a clear, high gloss coating. Pigmented and unpigmented films are used as primers, undercoatings or top coatings on porous or nonporous substrates, such as metal, cement, wood, wood fiber, mineral fibers, wall board and the like. In addition to paints and architectural coatings, those skilled in the art will appreciate that our polymer latices are further

useful as textile treatments, paper coatings, sealants and adhesives.

Example 1

In a 3 liter, 3 neck flask equipped with a mechanical stirrer, a condenser, an addition funnel, a thermometer, a heating mantel (having a temperature controller) and a nitrogen purge were added 758 g of deionized (DI) water, 72.9 g of a 28 percent aqueous solution of TRITON™ X-200, 3.75 g of ammonium persulfate and 3.0 g of sodium bicarbonate. The contents of the flask were stirred for 30 minutes at room temperature while a nitrogen purge was maintained. Inhibitor-free ethylacrylate, 226 g, (prepared by passing 500 g of ethylacrylate through a bed of 100 g of 34 to 74 micrometers (200-400 mesh) activated alumina was added to the flask all at once, stirring was maintained and heating was initiated. Approximately 45 minutes later, when the temperature reached 66°C., an exotherm occurred and the heating mantle was removed. A temperature maximum of 94°C. was obtained approximately 4 minutes later. The heating mantle was reapplied and the heat was increased to the flask. After 20 minutes, the temperature had stabilized at 70°C. An additional 225 g of ethylacrylate were added dropwise over a two hour period while the temperature was maintained at 70°C. Next a solution of 12.56 g of divinyltetramethyldisiloxane in 225 g of ethylacrylate was added to the flask dropwise over a two hour period. After this solution had been added, the emulsion was further heated with stirring for 60 minutes while the temperature was maintained at 70°C. The heating mantel was removed and the emulsion was allowed to cool to room temperature with stirring. The contents of the flask were filtered through a 149 µm polypropylene filter and later heated to 50°C. for 30 minutes in vacuo using a rotary evaporator. Thereafter, 7.8 g of material remained in the filter and 98.4 g of condensate (including water) were collected in the evaporator receiver. The recovered emulsion weighed 1351 g and it had a non-volatile content of 49.5 wt%. The emulsion had a mean particle size of 168 nm and 99 percent of the particles were less than 257 nm, determined by a light scattering method (NIACOMP). The emulsion had a viscosity of 32.0 mPa • s (cps) (Brookfield, #1 spindle, 60 RPM) and a minimum film forming temperature below -5°C. This latex consisted of an emulsion of polyethylacrylate containing 1.0 mole percent of divinyltetramethyldisiloxane.

Films were cast by pouring 11 g of this emulsion into a 100 mm diameter polystyrene Petri dishes that had been previously coated with a thin film of silicone grease. The emulsion films were allowed to dry at ambient conditions for 7 days after which tensile properties were determined (Instron™). Swelling properties of the latex films were also determined using ethyl acetate as solvent. Swelling and tensile properties are given in Table I.

Example 2

Using the same procedure in Example 1, another latex was prepared such that it consisted of an aqueous emulsion of polyethylacrylate that contained 2.0 mole percent of divinyltetramethyldisiloxane. This emulsion was prepared using the same procedure of Example 1, except that 25.12 g of $(H_2C{=}CHMe_2Si)_2O$ was used. This latex had a mean particle size of 187 nm with 99 percent of the particles less than 330 nm and it had a non-volatile content of 48.9 percent by weight. The emulsion had a viscosity of 35.1 mPa • s (cps) (Brookfield, #1 spindle, 60 RPM) and a minimum film forming temperature below -5°C. Swelling and tensile properties of the films from this emulsion were also determined and they are presented in Table I.

Example 3

Using the procedure of Example 1, another emulsion was prepared such that it consisted of an aqueous emulsion of polyethylacrylate containing 1.0 mole percent of divinyltetramethyldisilazane. In this procedure, 12.47 g of $(H_2C{=}CHMe_2Si)_2NH$ was substituted for the $(H_2C{=}CHMe_2Si)_2O$. This emulsion had a mean particle size of 211 nm, with 99 percent of the particles less than 266 nm and it had a non-volatile content of 49.3 percent by weight. The emulsion had a viscosity of 23.0 mPa • s (cps) (Brookfield, #1 spindle, 60 RPM) and a minimum film forming temperature below -5°C. Swelling and tensile properties of films from this emulsion were determined and they are also presented in Table I.

Example 4

Using the procedure of Example 1, another emulsion was prepared such that it consisted of an aqueous of polyethylacrylate containing 2.0 mole percent of divinyltetramethyldisilazane. In this procedure, 24.94 g of $(H_2C{=}CHMe_2Si)_2NH$ was substituted for $(H_2C{=}CHMe_2Si)_2O$. This emulsion had a mean particle size of 244 nm, with 99 percent of the particles less than 365 nm and it had a non-volatile content of 48.7 percent by weight. The emulsion had a viscosity of 18.0 mPa • s (cps) (Brookfield, #1 spindle, 60 RPM) and a minimum film forming temperature below -5°C. Swelling and tensile properties of films from this emulsion were also determined and presented in Table I.

Example 5

Using a modified procedure of Example 1, another latex was prepared such that it consisted of an aqueous emulsion of polyethylacrylate containing 0.5 mole percent of methylvinylcyclotrisiloxane. In this procedure, the amount of sodium bicarbonate was doubled (6 g added) and 2.9 g of $(H_2C{=}CHMeSiO)_3$ was substituted for $(H_2C{=}CHMe_2Si)_2O$. During preparation of this latex, 7.2 g of coagulum were collected by filtration, 118.9 g of volatiles was collected by stripping and 1323 g of latex were recovered. The latex had a mean particle size of 192 nm, with 99 percent of the particles less than 286 nm and it had a non-volatile content of 50.4 percent by weight. The emulsion had a viscosity of 30.4 mPa • s (cps) (Brookfield, #1 spindle, 60 RPM) and a minimum file forming temperature below -5°C. Swelling and tensile properties of films from this emulsion were determined and given in Table I.

Example 6

Using the procedure of Example 1, another latex was prepared such that it consisted of an aqueous emulsion of polyethylacrylate containing 0.5 mole percent of methylvinylcyclotrisiloxane. In this procedure, 2.9 g of $(H_2C{=}CHMeSiO)_3$ were substituted for $(H_2C{=}CHMe_2Si)_2O$. During preparation, 8.5 g of coagulum were collected by filtration, 110.4 g of volatiles were collected by stripping and 1328 g of latex were recovered. The latex had a mean particle size of 174 nm with 99 percent of the particles less than 255 nm and it had a non-volatile content of 49.9 percent by weight. The emulsion had a viscosity of 33.0 mPa • s (cps) (Brookfield, #1 spindle, 60 RPM) and a minimum film forming temperature below -5°C. Swelling and tensile properties of films from this emulsion were determined and reported in Table I.

Example 7

Using the procedure of Example 1, another latex was prepared such that it consisted of an aqueous emulsion of polyethylacrylate containing 2.5 mole percent of methylvinylcyclotrisiloxane. In this procedure, 14.5 g of $(H_2C{=}CHMeSiO)_3$ were substituted for the $(H_2C{=}CHMe_2Si)_2O$. During preparation, 6.4 g of coagulum were collected by filtration, 120.1 g of volatiles were collected by stripping and 1325 g of latex were recovered. The latex had a mean particle size of 173 nm, with 99 percent of the particles less than 264 nm and it had a non-volatile content of 50.7 percent by weight. The emulsion had a viscosity of 38.0 mPa • s (cps) (Brookfield, #1 spindle, 60 RPM) and a minimum film forming temperature below -5°C. Swelling and tensile properties of films from this emulsion were determined and reported in Table I.

Example 8

A comparative sample of an aqueous emulsion of ethyl acrylate, with no silicone, was prepared according to the following procedure. In a 3 liter, 3 neck flask equipped with a mechanical stirrer, a condenser, an addition funnel, a thermometer, a heating mantel (having a temperature controller) and a nitrogen purge were added 758 g of DI water, 72.9 g of TRITON™ X-200, 3.75 g of ammonium persulfate and 3.0 g of sodium bicarbonate. The contents of the flask were stirred for 60 minutes at room temperature while a nitrogen purge was maintained. 225 g of inhibitor-free ethylacrylate (prepared by passing 500 g of ethylacrylate through a bed of 100 g of 34 to 74 micrometers (200-400 mesh) activated alumina) were added to the flask all at once, stirring was maintained and heating was started. Approximately 30 minutes later, when the temperatures reached 73°C., an exotherm occurred and the heating mantle was removed. A temperature maximum of 93.5°C. was obtained approximately 3 minutes later. The heating mantle was reinstalled and heat was applied to the flask. After 20 minutes, the temperature had stabilized at 70°C. An additional 450 g of ethylacrylate were added dropwise over a 3.5 hour period while the temperature was maintained at 70°C. After the feed solution was added, the emulsion was heated with stirring for 60 minutes longer while the temperature was maintained at 70°C. The heating mantle was removed and the emulsion was allowed to cool to room temperature with stirring. The contents of the flask were filtered through a 149 µm polypropylene filter and later heated to 50°C for 30 minutes in vacuo using a rotary evaporator. 5.1 g of material remained in the filter and 93.7 g of condensate were collected in the evaporator receiver. The recovered emulsion weighed 1350 g and it had a non-volatile content of 49.4 wt%. The emulsion had a mean particle size of 168 nm and 99 percent of the particles were less than 248 nm, as determined by light scattering methods (NIACOMP). The emulsion had a viscosity of 30.7 mPa • s (cps) (Brookfield, #1 spindle, 60 RPM) and a minimum film forming temperature below -5°C. This latex consisted of an aqueous emulsion of polyethylacrylate.

Films were cast by pouring 11 g of emulsion into 100 mm diameter polystyrene Petri dishes that had been previously coated with a thin film of silicone grease. The emulsion films were allowed to dry at ambient conditions for 7 days after which tensile properties were determined (Instron™). Swelling properties of the latex films were also determined using ethyl acetate as solvent. Swelling and tensile properties are given in Table I.

TABLE I

silane	mole %	swell %	gel %	tensile		elong. %	Modulus 100%	
				psi	kPa		psi	kPa
none	0.0	--dissolved--		44	303.4	1032	19	131.0
$(H_2C=CHMe_2Si)_2O$	1.0	--dissolved--		41	282.7	578	19	131.0
$(H_2C=CHMe_2Si)_2O$	2.0	--dissolved--		34	234.4	508	15	103.4
$(H_2C=CHMe_2Si)_2NH$	1.0	5279	64.7	61	420.6	2133	17	117.2
$(H_2C=CHMe_2Si)_2NH$	2.0	4882	72.2	129	889.4	1994	16	110.3
$(H_2C=CHMeSiO)_3$	0.5	--dissolved--		47	324.0	1065	28	193.0
*$(H_2C=CHMeSiO)_3$	0.5	4410	80.1	81	558.5	851	28	193.0
$(H_2C=CHMeSiO)_3$	2.5	--dissolved--		43	296.5	427	31	213.7

* doubled the amount of $NaHCO_3$

Example 9

An aqueous silicone/butyl acrylate emulsion was prepared according to the following procedure. In a 3 liter, 3 neck flask equipped with a mechanical stirrer, a condenser, an addition funnel, a thermometer, a heating mantel (having a temperature controller) and a nitrogen purge were added 758 g of DI water, 72.9 g of TRITON™ X-200, 3.75 g of ammonium persulfate and 3.0 g of sodium bicarbonate. The contents of the flask were stirred for 30 minutes at room temperature while a nitrogen purge was maintained. Then, 225 g of inhibitor-free butylacrylate (prepared by passing 500 g of butylacrylate through a bed of 100 g of 34 to 74 micrometers (200-400 mesh) activated alumina) were added to the flask all at once. Stirring was maintained and heating was started. Approximately 30 minutes later, when the temperature reached 68°C., an exotherm occurred and-the heating mantle was removed. A temperature maximum of 88.5°C was obtained approximately 6 minutes later. The heating mantle was reinstalled and heat was applied to the flask. After 20 minutes, the temperature stabilized at 70°C. An additional 225 g of butylacrylate were added dropwise over a 1.5 hour period while the temperature was maintained at 70°C. Next, a solution of 9.8 g of divinyltetramethyldisiloxane in 225 g of butylacrylate was added to the flask dropwise over a 1.5 hour period. After all of the feed solution had been added, the emulsion was heated with stirring for 60 minutes longer while the temperature was maintained at 70°C. The heating mantle was removed and the emulsion was allowed to cool to room temperature with stirring. The contents of the flask were filtered through a 149 µm polypropylene filter and later heated to 50°C. for 30 minutes in vacuo using a rotary evaporator. 103.4 g of material remained in the filter and 107.6 g of condensate were collected in the evaporator receiver. The recovered emulsion weighed 1254.7 g and it had a non-volatile content of 47.2 percent by weight. The emulsion had a mean particle size of 153 nm and 99 percent of the particles were less than 260 nm, as determined by light scattering methods (NIACOMP). The emulsion had a viscosity of 31.0 mPa•s (cps) (Brookfield, #1 spindle, 60 RPM) and a minimum film forming temperature below -5°C. This latex consisted of an aqueous emulsion of polybutylacrylate containing 1.0 mole percent of divinyltetramethyldisiloxane.

Films were cast by pouring 11 g of emulsion into 100 mm diameter polystyrene Petri dishes that had been previously coated with a thin film of silicone grease. The emulsion films were allowed to dry at ambient conditions for 7 days after which swelling properties were determined using ethyl acetate as solvent. Swelling properties are given in Table II.

Example 10

Using the procedure of Example 9, another latex was prepared such that it consisted of an aqueous emulsion of polybutylacrylate that contained 2.0 mole percent of divinyltetramethyldisiloxane. Herein, 19.6 g of $(H_2C=CHMe_2Si)_2O$ were used. During preparation, 8.5 g of coagulum were collected by filtration, 108.7 g of volatiles were collected by stripping and 1354 g of latex were collected. The latex had a mean particle size of 143 nm, with 99 percent of the particles less than 198 nm and it had a non-volatile content of 49.7 percent by weight. The emulsion had a viscosity of 22.4 mPa•s (cps) (Brookfield, #1 spindle, 60 RPM) and a minimum film forming temperature below -5°C. Swelling properties of films from this emulsion were also determined using ethyl acetate as solvent and are given in Table II.

Example 11

Another latex was prepared such that it consisted of an aqueous emulsion of polybutylacrylate that contained 1.0

mole percent of divinyltetramethyldisilazane. This emulsion was prepared using the procedure of Example 9 except that 9.74 g of $(H_2C{=}CHMe_2Si)_2O$ were used. During preparation, 39 g of coagulum were collected by filtration, 112.8 g of volatiles were collected by stripping and 1312 g of latex were obtained. The latex had a mean particle size of 164 nm, with 99 percent of the particles less than 261 nm and it had a non-volatile content of 48.8 percent by weight. The emulsion had a viscosity of 43.0 mPa•s (cps) (Brookfield, #1 spindle, 60 RPM) and a minimum film forming temperature below -5°C. Swelling properties of films from this emulsion were also determined using ethyl acetate as solvent and are given in Table II.

TABLE II

silane	mole %	% swell	% gel
none	0.0	--dissolved--	
$(H_2C{=}CHMe_2Si)_2O$	1.0	--dissolved--	
$(H_2C{=}CHMe_2Si)_2O$	2.0	--dissolved--	
$(H_2C{=}CHMe_2Si)_2NH$	1.0	5323	84.3

Example 12

100 g of the emulsion of Example 1 were weighed into a 500 ml jar equipped with a mechanical stirrer. Next, 0.5 g of methyltrimethoxysilane were added to the emulsion with stirring followed by 0.5 g of a 50 percent aqueous emulsion of dioctyltindioctoate. The latex was stirred for 3 minutes after addition of silane and tin catalyst. This emulsion consisted of a latex of polyethylacrylate/0.5 mole percent $(H_2C{=}CHMe_2Si)_2O$, 0.5 part of $MeSi(OMe)_3$ and 0.25 part of dioctyltindilaurate (parts based on 100 parts of polymer dry weight). Films of this latex were cast by the procedure of Example 1 and swelling properties were determined using ethyl acetate as solvent. Using the same procedure, $MeSi(OCH_3)_3$ and tin catalyst were added to the emulsions described in Examples 2-4 and Example 8. Swelling properties of these latex films are given in Table III.

TABLE III

latex from	phr $CH_3Si(OCH_3)_3$ + Sn catalyst*		% swell	% gel
Example 8 (control)	0.0	0.0	-- dissolved--	
Example 8 (control)	1.0	0.25	-- dissolved--	
Example 1	0.0	0.0	-- dissolved--	
Example 1	1.0	0.25	-- dissolved--	
Example 2	0.0	0.0	-- dissolved--	
Example 2	1.0	0.25	4534	75.1
Example 3	0.0	0.0	5279	64.7
Example 3	1.0	0.25	3170	70.4
Example 4	0.0	0.0	4882	72.2
Example 4	1.0	0.25	2734	71.8
phr = parts per hundred parts of polymer solids. Sn catalyst = dibutyltindilaurate also as phr on solids basis.				

Claims

1. A method for producing a silicone organic copolymer latex, comprising the steps of:

   forming an emulsion comprising an organic monomer, water and a surfactant, such that the organic monomer forms the discontinuous phase,

copolymerizing the organic monomer with a crosslinker, wherein the crosslinker has the formulae:

$$Q_nR_{3-n}Si\text{-}X\text{-}(RQSiX)_z(R_2SiX)_y\text{-}SiR_{3-n}Q_n$$

or

$$\overline{\left[(RQSiX)_{z'}(R_2SiX)_{y'}\right]}$$

where:

Q independently represents an allyl, vinyl, hexenyl, acryloxy or methacryloxy radical;
X is O or NR; and
R is independently a hydrogen atom or an alkyl, aryl and alkyl/aryl group having 1 to 8 carbon atoms;
$\underline{n}$ = 0, 1, 2 or 3;
$\underline{z}$ = 0 to 200;
$\underline{y}$ = 0 to 200, with the proviso that if $\underline{n}$=0, then $\underline{z} \geq 1$;
$\underline{z}'$= 1 to 50; and
$\underline{y}'$= 0 to 50, with the proviso that

$$\underline{z}' + \underline{y}' \geq 3.$$

2. The method of claim 1 wherein surfactant is added in an amount of 0.25 to 7.0 parts by weight per 100 parts by weight of organic monomer.

3. The method of claim 1 wherein initiator is added in an amount of 0.1 to 2.0 parts by weight per 100 parts by weight of organic monomer.

4. The method of claim 1 wherein water is added in an amount of 60 to 400 parts by weight per 100 parts by weight of organic monomer.

5. The method of claim 1 wherein the crosslinker comprises 0.1 to 20% by weight of the total polymer emulsion.

6. The method of claim 1 comprising an additional step of adding a filler after said copolymerization.

7. The method of claim 1 comprising the additional step of adding a buffer during the copolymerization step.

8. The method of claim 1 comprising the additional step of adding a chain transfer agent during the copolymerization step.

9. The method of claim 1 wherein the pH of the composition is maintained at 7 or greater during the copolymerization step.

10. The method of claim 1 wherein the pH of the composition is maintained below 7 during the copolymerization step.

11. The method of claim 1 comprising the additional step of adding an organotin catalyst after the copolymerization step.

12. The method of claim 1 which also includes an additive of the formulae $R_aSiX'_{4-a}$ or $X'_{3-a}R_aSiO\text{-}(R_2SiO)_n\text{-}SiR_aX'_{3-a}$ where R is independently the same or different monovalent hydrocarbon group having from 1-8 carbon atoms; X' is any hydrolyzable group; and $\underline{a}$ is either 0, 1 or 2.

13. The silicone organic copolymer latex obtainable by the method of any of the claims 1-12.

14. The method of claim 13 comprising the additonal step of removing water.